Scaling laws for the photo-ionisation cross section of two-electron atoms

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The cross sections for single-electron photo-ionisation in two-electron atoms show fluctuations which decrease in amplitude when approaching the double-ionisation threshold. Based on semiclassical closed orbit theory, we show that the algebraic decay of the fluctuations can be characterised in terms of a threshold law $\sigma \propto |E|^{\mu}$ as $E \to 0_-$ with exponent μ obtained as a combination of stability exponents of the triple-collision singularity. It differs from Wannier's exponent dominating double ionisation processes. The details of the fluctuations are linked to a set of infinitely unstable classical orbits starting and ending in the non-regularisable triple collision. The findings are compared with quantum calculations for a model system, namely collinear helium.

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Recent experimental progress has significantly improved the energy resolutions of highly excited two electron states below [1, 2] and above [3] the double ionisation threshold $E = 0$. Near the threshold, electron-electron correlation effects become dominant which are directly observable in total and partial cross sections, see [4, 5, 6] for recent reviews; an example is Wannier's celebrated threshold law for double ionisation [7] confirmed experimentally in [8]. For $E < 0$, two-electron atoms exhibit a rich resonance spectrum while the classical dynamics of this three-body Coulomb problem becomes chaotic. Approaching the double ionisation threshold from below has thus proved challenging [6] and recent experimental and theoretical efforts still only reach single-ionisation thresholds I_N with $N \leq 15$ [1, 2, 9]. Semiclassical methods need to address the chaotic nature of the classical dynamics which is dominated by the complex folding patterns of the stable/unstable manifolds of the triple collision [10]. Due to the high dimensionality of the system semiclassical applications have been restricted to subsets of the full spectrum and again small N values [6].

In this letter, we show that the fluctuations in the total cross section for single electron photo-ionisation below the three-particle breakup energy decays algebraically with an exponent determined by the triple collision singularity *different* from Wannier's exponent. Writing the cross section in dipole approximation [11, 12], we obtain

$$\sigma(E) = -4\pi\,\alpha\,\hbar\omega\,\Im\langle D\phi_i|G(E)|D\phi_i\rangle \tag{1}$$

where ϕ_i is the wave function of the initial state and $D = \boldsymbol{\pi}\cdot(\mathbf{r}_1 + \mathbf{r}_2)$ is the dipole operator with π, the polarisation of the incoming photon and $\mathbf{r}_j$, the position of electron j. Furthermore, $G(E)$ is the Green function of the system at energy $E = E_i + \hbar\omega$ and $\alpha = e^2/\hbar c$. Note that we work in the infinite nucleus mass approximation, that is, the position of the nucleus is fixed at the origin.

By expressing the Green function semiclassically in terms of classical trajectories [11], fluctuations in the cross section of hydrogen-like atoms in external fields have been analysed successfully using *closed orbit theory* (COT) [11, 12]. In the semiclassical limit, the support of the wave function ϕ_i shrinks to zero relative to the size of the system reducing the integration in (1) to an evaluation of the Green function at the origin. This is strictly valid only for potentials sufficiently smooth at the origin, corrections due to diffractive scattering at the central singularity give additional contributions often treated in quantum defect approximation [13, 14]. The situation is different for two-electron atoms where the dynamics near the origin is dominated by the non-regularisable triple collision singularity. Closed orbit theory has been used to analyse experimental photoabsorbtion spectra of helium with and without external fields [13, 15] for highly asymmetric states; accompanying theoretical considerations treat the system in a single electron approximation thus not considering the triple collision dynamics which becomes important for doubly-excited resonances.

In the following, we will discuss a COT treatment of two-electron atoms explicitly including the triple collision dynamics when approaching the limit $E \to 0_-$. Introducing the hyperradius $R = (\mathbf{r}_1^2 + \mathbf{r}_2^2)^{1/2}$, we fix R_0 such that a surface Σ defined as $R = R_0$ encloses the support of initial state ϕ_i. The surface Σ naturally leads to a partition of the configuration space into physically distinct regions. In particular, quantum contributions to (1) from the inner region are insensitive to the total energy. Contributions from the outer region test the full scale of the classically allowed region of size $|E|^{-1}$ and will be responsible for the resonance structures near the double ionisation threshold $E = 0$. Following Granger and Greene [16], we write the photo-ionisation cross section (1) in terms of local scattering matrices, that is,

$$\sigma = 4\pi^2\alpha\hbar\omega\,\Re\left[d^\dagger\left(1 - S^\uparrow S^\downarrow\right)^{-1}\left(1 + S^\uparrow S^\downarrow\right)d\right] \tag{2}$$

$$= 4\pi^2\alpha\hbar\omega\,\Re\left[d^\dagger\left(1 + 2S^\uparrow S^\downarrow + 2(S^\uparrow S^\downarrow)^2 + \dots\right)d\right] \tag{3}$$

Here, $S^\downarrow$ is a core-region scattering matrix which maps amplitudes of waves coming in at Σ onto amplitudes of

the wave components going out at Σ; it thus contains all the information about the correlated two-electron dynamics near the nucleus. Likewise, $S^{\uparrow}$ describes the wave dynamics of the two-electron wave function emanating from and returning to Σ and thus picks up long-range correlation in the exterior of Σ. Furthermore, d is the atomic dipole vector, $d_n(E) =< \Psi_n^{\downarrow}(E)|D\phi_i >$ with $\Psi_n^{\downarrow}(E)$ being the nth linearly-independent energy-normalised solution of the Schrödinger equation inside Σ with incoming wave boundary conditions at Σ [16]. This type of scattering formulation was independently developed in [17] for general surfaces Σ, for a semiclassical formulation, see [18]. The series expansion (3) was exploited in [13, 14, 19] in order to include core-region scattering or quantum defect effects in COT.

For the wave dynamics inside Σ, the double ionisation threshold $E = 0$ is irrelevant and the core-region scattering matrix $S^{\downarrow}$ as well as the dipole vector d vary smoothly across $E = 0$; they can be regarded as constant for energies sufficiently close to the threshold. The information about the increasing number of overlapping resonances near the threshold is thus largely contained in $S^{\uparrow}$.

Semiclassical approximations for the quantities introduced above are valid in the outer-region $R > R_0$. The long-range scattering matrix, $S^{\uparrow}$, can thus be treated semiclassically while d and $S^{\downarrow}$ demand a full quantum treatment. The semiclassical representation of $S^{\uparrow}$ in position space reads [16, 17, 18]

$$S^{\uparrow}(x, x', E) \approx (2\pi i\hbar)^{-\frac{f-1}{2}} \sum_j |M_{12}|_j^{-1/2} e^{i\frac{S_j}{\hbar} - i\frac{\pi\nu_j}{2}}\ , \quad (4)$$

where the sum is taken over all classical paths j connecting points x and x' on Σ without crossing Σ; $S_j(E)$ denotes the action of that path, ν_j is the Maslov index and $f = 4$ is the dimension of the system for fixed angular momentum. Furthermore, $|M_{12}|_j^{-1/2} = |\partial^2 S_j(x, x')/\partial x\partial x'|^{1/2}$, where M_{12} is a (3×3) sub-matrix of the 6-dim. Monodromy matrix describing the linearised flow near a trajectory. Note that due to the strong instability of the classical dynamics near the triple collision, these matrix elements become singular for triple collision orbits (TCO) starting from or falling into the triple collision $R = 0$. It is thus important here that trajectories contributing to (4) start at a fixed hyper-radius $R_0 > 0$ away from the triple collision [20].

Making use of the scaling properties of the classical dynamics, we introduce the transformation [21]

$$\mathbf{r} = \tilde{\mathbf{r}}/|E|; \quad \mathbf{p} = \sqrt{|E|}\tilde{\mathbf{p}}; \quad S = \tilde{S}/\sqrt{|E|}, \quad \mathbf{L} = \tilde{\mathbf{L}}/\sqrt{|E|}$$

where $\tilde{\mathbf{r}}, \tilde{\mathbf{p}}$ corresponds to coordinates and momenta at fixed energy $E = -1$ and $\mathbf{L}$ is the total angular momentum. Expressing $\mathbf{L}$ in scaled coordinates, we have $\tilde{\mathbf{L}} \to 0$ as $E \to 0$ and can thus restrict the analysis to the three degrees of freedom subspace $\tilde{L} = 0$ (for fixed L) [10].

In scaled coordinates, the inner-region shrinks according to $\tilde{R}_0 = |E|R_0 \to 0$ for $E \to 0_-$, and the part of the dynamics contributing to $S^{\uparrow}$ in (4) is formed by trajectories starting and ending closer and closer to the triple collision $R = 0$ as $|E| \propto \tilde{R}_0 \to 0$. TCOs only occur in the so-called eZe space [10], a collinear subspace of the full three body dynamics where the two electrons are on opposite sides of the nucleus [21]. As $\tilde{R}_0 \to 0$, only orbits coming close to the eZe space can start and return to $\tilde{\Sigma}$ and they will do so in the vicinity of a *closed triple collision orbit* (CTCO) starting and ending exactly in the triple collision. The dynamics in the eZe space is relatively simple as it is conjectured to be fully chaotic with a complete binary symbolic dynamics. In particular, for every finite binary symbols string there is a CTCO, the shortest being the so-called Wannier orbit (WO) of symmetric collinear electron dynamics. Furthermore TCOs escape from or approach the triple collision at $R = 0$ always symmetrically along the $r_1 = r_2$ axis in the eZe space, that is, along the WO [22]. This universality will be exploited below when treating the energy-dependence of M_{12} in (4).

Returning to the cross-section (2), we write $\sigma = \sigma_0 + \sigma_{fl}$, where we identify the smooth contribution σ_0 with the leading term in the series expansion (3). The main contribution to the fluctuating part of the cross section σ_{fl} is contained in $S^{\uparrow}$ which in semiclassical approximation (4) can be expressed in terms of orbits returning to $\tilde{\Sigma}$ once; multiple traversals of $\tilde{\Sigma}$ represented by $\left(S^{\uparrow}S^{\downarrow}\right)^k$ with $k \geq 2$ will give sub-leading contributions in the semiclassical limit $E \to 0_-$ due to the unstable dynamics near the triple collision. Furthermore, swarms of trajectories starting on $\tilde{\Sigma}$ and returning to $\tilde{\Sigma}$ will do so close to the eZe subspace and thus in the neighbourhood of a CTCO with actions and amplitudes approaching those of the CTCO trajectory as $\tilde{R}_0 \to 0$. The fluctuating part can thus in leading order be written in the form

$$\sigma_{fl}(E) \approx \Re \sum_{\mathrm{CTCO}_j} A_j(E) e^{iz\tilde{S}_j} \quad (5)$$

with

$$A_j(E) \propto |M_{12}(E)|_j^{-1/2} = |E|^{9/4} |\tilde{M}_{12}(\tilde{R}_0)|_j^{-1/2} \quad (6)$$

and $z = 1/\hbar\sqrt{|E|}$. In (5), the sum is taken over all CTCO's j starting and ending at $\tilde{\Sigma}$. Note that the stability $\tilde{M}_{12}(\tilde{R}_0)$ in scaled coordinates depends on energy implicitly through the scaled radius $\tilde{R}_0(E) = |E|R_0$. As $E \to 0_-$, $\tilde{M}_{12}$ picks up additional contributions of parts of the CTCO closer and closer to the triple collision. Asymptotically, all CTCOs approach the triple collision along the WO and the contributions to M_{12} become orbit-independent. The R-dependence for the Monodromy matrix of the WO can for small $\tilde{R}$ be obtained *analytically* [23] leading to

$$|\tilde{M}_{12}(\tilde{R}_0)| \propto |\tilde{R}_0|^{-2\mu+9/2} \text{ for } \tilde{R}_0 \to 0 \quad (7)$$

with exponent

$$\mu = \mu_{eZe} + 2\mu_{wr} = \frac{1}{4}\left[\sqrt{\frac{100Z-9}{4Z-1}} + 2\sqrt{\frac{4Z-9}{4Z-1}}\right]. \quad (8)$$

Thus, in unscaled coordinates, M_{12} in (6) diverges which is a direct consequence of the non-regularisability of the triple collision acting as an infinitely unstable point in phase space; details will be presented in [23]. The exponent μ in (8) is universal for all CTCOs and consists of two components: μ_{eZe} is related to the linearised dynamics in the eZe space and μ_{wr} picks up contributions from two equivalent expanding degrees of freedom orthogonal to the eZe space in the so-called Wannier ridge (WR). The latter is the invariant subspace of symmetric electron dynamics with $|r_1| = |r_2|$ at all times [21]. The fluctuations in the photo-ionisation cross section thus vanish in amplitude as $E \to 0_-$ according to

$$\sigma_{fl}(E) \propto |E|^{\mu}\, \Re \sum_{\mathrm{CTCO}_j} a_j e^{iz\tilde{S}_j} \quad (9)$$

where the rescaled amplitudes $a_j = |E|^{-\mu} A_j$ depend only weakly on E. These amplitudes contain contributions from the linearised dynamics along the orbit far from Σ as well as information about the inner quantum region $R < R_0$ via the dipole vector d and the core-region scattering matrix $S^{\downarrow}$. Furthermore, multiple traversals of Σ contained in $\left(S^{\uparrow}S^{\downarrow}\right)^k$ with $k \geq 2$ in (3) approach the triple collision k times from the semiclassical side and will thus contribute at lower order with weights scaling at least as $A_{kj} \sim |E|^{k\mu}$. The exponent μ in (8) is different from Wannier's exponent μ_w with

$$\mu_w = \frac{1}{4}\sqrt{\frac{100Z-9}{4Z-1}} - \frac{1}{4}. \quad (10)$$

One obtains, for example, $\mu = 1.30589...$ compared to $\mu_w = 1.05589...$ for helium; the WR contributes to the decay for $Z > 9/4$ when μ_{wr} is real.

The exponent μ can be interpreted in terms of stability exponents of the triple collision singularity. Using an appropriate scaling of space and time by, for example, employing McGehee's technique [22], the dynamics near the singularity is dominated by two unstable fixed points in scaled phase space, the *double escape point* (DEP) and the *triple collision point* (TCP). In unscaled coordinates, these fixed points correspond to the WO at energy $E = 0$, that is, the DEP is the trajectory of symmetric double escape while the TCP corresponds to the symmetric triple collision and is the time reversed of the DEP. The triple collision itself can be mapped onto the classical dynamics at $E = 0$; likewise, $\tilde{R}_0 = |E| R_0$ acts as a parameter measuring the closeness to the $E = 0$ manifold which contains the fixed points, see [10, 22]. Most classical trajectories emerging from $\tilde{\Sigma}$ in the vicinity of the triple collision $\tilde{R} = 0$ will lead to immediate ionisation of one electron carrying away a larger amount of kinetic energy. Only a fraction of orbits starting on $\tilde{\Sigma}$ near the WO will enter a chaotic scattering region; the WO at $E < 0$ thus acts as an unstable direction of the DEP, U_D^{wo}, with a stability exponent $\lambda_{U_D}^{wo}$. From there, they can return to the triple collision region and thus approach the surface $\tilde{\Sigma}$ again along the WO, that is, along the stable direction S_T^{wo}. The transition from the DEP into the chaotic scattering region and from this scattering region to the TCP is limited by the least stable eigendirections of the fixed points in each of the invariant subspaces (eZe or WR) perpendicular to the WO.

Trajectories leaving $\tilde{\Sigma}$ along the WO in the eZe space diverge from the WO along an unstable direction U_D^{eZe} with a stability exponent $\lambda_{U_D}^{eZe}$. Competition of the instability in U_D^{wo} with that in U_D^{eZe} determines the fraction Δ_{eZe}^D of orbits entering the chaotic scattering region. By using methods as in [10, 24], one finds that

$$\Delta_{eZe}^D \propto \tilde{R}_0^{\lambda_{U_D}^{eZe}/\lambda_{U_D}^{wo}} = \tilde{R}_0^{\mu_w} \quad (11)$$

with exponent equal to Wannier's exponent (10). For the cross section (1), information about the phase space region returning from the chaotic scattering region to the surface $\tilde{\Sigma}$ along the WO is also needed. While approaching $\tilde{\Sigma}$, these orbits are deflected away from the triple collision along an unstable direction U_T^{eZe} of the TCP fixed point. The fraction of orbits reaching the surface $\tilde{\Sigma}$ among those leaving the chaotic scattering region scales thus as in (11) now with exponent $\lambda_{U_T}^{eZe}/|\lambda_{S_T}^{wo}|$. Similar mechanisms apply for the WR dynamics.

The fraction Δ of two-electron trajectories making the transition from $\tilde{\Sigma}$ back to $\tilde{\Sigma}$ can thus in the limit $E \to 0_-$ be estimated in terms of the stability exponents of the fixed points, also referred to as Siegel exponents [24] in celestial mechanics. One obtains $\Delta \propto \tilde{R}_0^{2\mu}$ with μ as in (8) which can be written as

$$\mu_{eZe} = \frac{1}{2}\left(\frac{\lambda_{U_D}^{eZe}}{\lambda_{U_D}^{wo}} + \frac{\lambda_{U_T}^{eZe}}{|\lambda_{S_T}^{wo}|}\right); \quad \mu_{wr} = \frac{1}{2}\left(\frac{\lambda_{S_D}^{wr}}{\lambda_{U_D}^{wo}} + \frac{\lambda_{U_T}^{wr}}{|\lambda_{S_T}^{wo}|}\right);$$

for the actual values of the stability exponents λ, see [7, 10]. The mean amplitude of the fluctuations in the quantum signal is thus asymptotically related to the fraction of phase space volume starting and ending at $\tilde{R}_0$.

A numerical study of the full three-body quantum problem is still out of reach for energies $E < I_N$ with $N \sim 15$ [1, 9]; we therefore chose a model system, namely eZe collinear helium first studied quantum mechanically in [25]. We calculated the cross section (1) directly in a large set of basis functions using the method of complex rotation and obtained a converged signal for $N \sim 55$. Semiclassically, we consider now the dynamics in the eZe space alone, which contains all the important parts regarding the algebraic decay in the fluctuations. The number of basis functions used are scaled with energy to cover a fixed scaled region in $\tilde{R}$ containing CTCOs with $\tilde{S}/2\pi \leq 20$. Adopting the basis functions used by

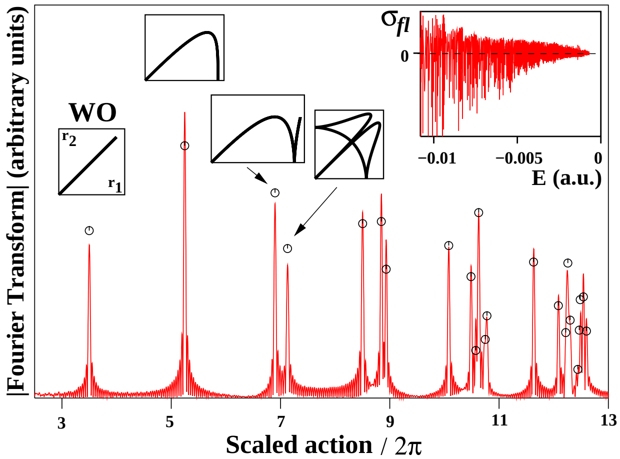

FIG. 1: The Fourier spectrum of the fluctuating part of the eZe cross section rescaled according to (12); the circles denote the position $\tilde{S}_j$ and (relative) size of $|M_{12}|_j^{-1/2}$ for CTCO's with $\tilde{S}/2\pi < 13$. Corresponding trajectories in configuration space are shown for the first 4 peaks. Inset: σ_{fl} for $N \leq 52$.

Püttner *et al* [1] leading to a strongly banded Hamiltonian matrix, it is possible to increase the basis size to 10^6. Starting with an odd initial state ϕ_i, we obtain the cross section for the even parity eZe spectrum; its fluctuating part after numerically subtracting a smooth background is shown in Fig. 1. The numerical value of the exponent μ is determined by rescaling the signal according to

$$F(z) = |E|^{-\mu}\sigma_{fl}(z)/\hbar\omega \qquad (12)$$

and testing the stationarity of the Fourier transform of $F(z)$ in different energy windows [23]. The best value thus obtained is $\mu = 1.306 \pm 0.035$ in good agreement with the theoretical prediction (8). (Note that the real parts of the exponents for 3-dim. helium and for eZe helium coincide as $\Re\mu_{wr} = 0$). Furthermore, the peaks in the Fourier transform can be associated one-by-one with CTCO's in the eZe system, see Fig. 1. We do not observe peaks associated with the concatenation of different CTCO's or repetitions of single CTCO's. This is consistent with the expected suppression of orbit contributions traversing Σ more than once as discussed earlier. Furthermore, we calculated the geometrical contribution to the coefficients a_j in (9) directly from the matrix-elements M_{12} by scaling out the leading order divergence; a clear correlation with the peak heights can be seen in Fig. 1. Quantum contributions from the core region are thus indeed roughly the same for all CTCOs.

In conclusion, we show that the fluctuations in the total photo-ionisation cross section below the double ionisation threshold follow an algebraic law with a novel exponent which can be written in terms of stability exponents of the triple collision. Our findings are verified numerically for a collinear model systems; we furthermore predict that the algebraic decay law is valid for the physically relevant 3 dimensional cases with an additional contribution from the WR dynamics for $Z > 9/4$. Our findings will provide new impetus for experimentalists and theoreticians alike to study highly doubly excited states in two-electron atoms.

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